SCIENCE FOR CERAMIC PRODUCTION

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LOCAL COMPACTION AREAS IN SINTERING OF CERAMICS AND STRUCTURAL REPRODUCIBILITY

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An analysis of fracture surfaces is suggested for assessment of local compaction areas in non-fired and sintered preforms. The analysis of samples made of highly disperse aluminum oxide by extrusion, plastic molding, and casting and heat-treated at different temperatures indicated that local compaction areas are formed in the molding stage, and the nature of the fractures remains similar until a high density of the material is reached. In the context of synergetics, the phenomenon of inherited structure in ceramics is attributed to the controlling effect of internal factors (of the previous structure) at the points of bifurcation on the system's evolution. A hypothesis is put forward that levelling of the fracture relief in sintered samples corresponds to the temperature region of bifurcation of the sintered system.

In drying and sintering of preforms made of highly disperse powders, some local compaction is observed, whose density is higher than that of the adjacent areas of a preform of a fired article. The reason for the emergence of these compacted areas is the tendency of the powder particles toward a local decrease in their surface energy through aggregation.

The density in the local compaction areas increases, and at the boundaries of these areas it decreases. In firing, crystals start growing inside the compacted areas, and pores which are hard to remove in the final stage of sintering grow between the compacted areas. As a consequence, ceramics after firing can contain large crystals and pores, which impairs their mechanical properties.

The local compacted areas are the consequence of the irreversibility and nonequilibrium of the processes which take place in ceramics production. According to contemporary concepts, all natural processes are irreversible and nonequilibrium [1]. A system perceived as a part of space separated from the environment by an actual or imaginary boundary evolves in a stability – instability – stability sequence, or, in other words, attractor – bifurcation – attractor sequence [2, 3]. The entropy of the system can decrease, as well as increase, i.e., self-organization takes place. The processes of self-organization, stability, and disintegration of structures in systems are studied in synergetics [1] ("synergetics" in Greek means "acting together").

Real systems are combinations of order and chaos. When a system is in a stable state, negative feedback acts in it. According to the Le Chatelier – Brown principle, a system creates structures which oppose external actions. When a system is in an unstable state, positive feedback is observed, and the system acquires increased sensitivity to internal fluctuations and external perturbations. The probabilistic aspect of the matter is manifested in bifurcation. Real systems are combinations of order and chaos, and can be described using fractal geometry [1]. The processes in open systems are determined by the degree of their nonequilibrium, i.e., the intensity of their material exchange with the environment.

The purpose of the present work is to study the effect of local compaction on the change in the structure of ceramics in heat treatment and to develop a method for monitoring this phenomenon. The description of local compaction processes in ceramic preforms in the course of molding and subsequent heat treatment will be offered from the standpoint of synergetics.

Ceramic production processes simultaneously proceed at diferent levels: the sublevel, the microlevel, and the macrolevel [2]. Owing to the probabilistic nature of the behavior of a system in bifurcations, finite states cannot be reproduced with absolute precision. Were it not for the possibility of accomplishing sufficiently similar states, the development of stable technologies would have been impossible. However, the results can be close enough, which allows production of articles very similar in quality.

The properties of a system (a ceramic article) can be regulated by using internal or external actions which should ex-

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ceed the noise level [3]. The internal actions include the structural changes in the earlier stages, such as granulation, granular composition of powder, etc., which have a determining effect (are inherited) on the subsequent stages. The external effects consist in changes in molding, drying, and firing procedures, such as variations in pressure, gas medium, temperature regime, etc. Noises are interanl and external effects which cannot be controlled.

The local compaction process and its effect on the product structure are of great significance for the technology of highly disperse powders [4]. The substantial surface energy of particles contributes to a high degree of nonequilibrium of the process of a decrease in the surface energy through aggregation and often makes it spontaneous and hard to control. It can result in the emergence of structures consisting of crystals of different sizes, including large ones, and containing relatively large pores. Therefore, the study of the evolution of local compaction, especially in the sintering stage, is quite important and necessary for current technology.

An analysis of the nature of fractures resulting from destruction of samples was recognized as the most promising method of control over local compaction. The strength of the material inside the compacted areas should be slightly higher than at the boundaries of these areas. If a crack does not move too quickly, it should mainly move along the boundaries of the compacted areas. At a higher velocity, a crack can pass not only along the boundaries but across the compacted areas as well. It was decided to study the fracture surfaces produced by destruction of preforms in three-point bending. The conditions of preform manufacture are listed in Table 1.

Samples 1 were dried and then heat-treated at temperatures ranging from 500 to 1700°C. After a preassigned temperature was reached, the furnace was switched off and the samples were cooled together with the furnace. Samples were fired for 12 h at the temperature of 1700°C. After drying and heat treatment the samples were fractured, and the fracture surface was analyzed with a binocular microscope.

The low strength of the non-fired samples and samples fired at a low temperature was the reason for a low energy of the moving crack. In these circumstances, the crack mainly migrated along the boundaries of the denser areas. After firing at high temperatures, the preform acquired a high strength, which resulted in the high energy and speed of crack movement. In this case, the sensitivity of the crack movement path to local compaction areas perceptibly decreased. The fracture relief became smoother. Apparently, it is necessary to make a sharp nick in a sample and to analyze the area immediately adjacent to the nick apex where the crack has not had time to acquire a high speed.

The analysis of fractures was performed at different illumination angles in order to make the relief contour more contrasting. Rotation of the sample in combination with variation of the illumination angles revealed the textures, i.e., the regularities in the arrangement of the fracture elements. The main problem is to estimate the compacted areas by their imprint on the fracture. It is clear that elevations and hollows have to be smaller than the structural element whose imprint they represent, since the probability of the crack passing precisely in its middle is low. However, assuming that the ratio of the average-sized imprint element on the fracture surface to the actual element remains sufficiently stable, one can estimate in relative values the changes in locally compacted areas judging from the changes in the imprint size.

The results of binocular-microscopic analysis of fractures are given in Table 2. Samples 1 were dried at room temperature and at 100°C. The elevations and hollows were observed on the fracture surfaces. With a sample positioned at a certain angle to the light source, it could be seen that the elevations are arranged in rows. The rows are oriented mostly perpendicular to the direction of force application and are probably the consequence of plastic deformation of the mixture in molding. They were most noticeable in the samples made of GLMK powder molded at a a pressure of 150 MPa. With

TABLE 1

Sample	Precursor powders	Binder type	Binder content, wt. %	Sieve number for powder	Molding pressure, MPa
1	$Al(OH)_3$*	Water	10.0	05	50
2	The same	PVA	16.8	1	100
3	–"–	The same	28.0	–	–
4	GLMK**	Water	5.0	1	30
5	The same	PVA	16.8	1	150

* Corundum obtained by calcination of $Al(ON)_3$, crystal size below 1 μm.
** Corundum with addition of 0.25 (wt. %) MgO, crystal size 1 – 2 μm.

TABLE 2

Heat treatment temperature, °C	Primary aggregates, size of hollows, μm, in samples			Secondary compactions, size of hollows, μm, in samples			Linear shrinkage in samples, %		
	1	2	3	1	2	3	1	2	3
20	60	60	–	150	–	–	–	–	–
100	60	60	–	60	150	600	–	–	–
500	60	60	25 – 30	60	150	300	–	–	–
700	60	60	25 – 30	60	150	150	–	–	–
1000	60	60	25 – 30	60	60	25 – 30	–	–	–
1100	60	60	25 – 30	60	60	600	–	–	–
1300	30	–	25 – 30	30	300 – 400	450	3.5	3.5	3.0
1500	25	–	–	25	300 – 400	150	9.7	9.4	11.0
1700	–	–	–	–	–	–	24.7	22.5	26.0

an increase in the molding pressure, orientation virtually disappeared. In the samples dried at the temperature of 100°C, the rows were less evident, and the size of the hollows was smaller (60 – 75 μm) than after drying at 20°C (60 – 150 μm). The degree of nonequilibrium of the drying process at 100°C is higher than at 20°C. This agrees with the fact that an increase in the degree of nonequilibrium reduces the number of structural elements in the system [1].

After heat treatment at the temperatures of 500, 700, 1000, and 1100°C, no shrinkage was observed in the samples. The fracture reliefs were very similar. In samples molded at a pressure of 150 MPa, rows of elevations and hollows were observed. The prevailing size of the hollows and elevations was about 60 μm. After heat treatment at 1300, 1500, and 1700°C, the shrinkage of the samples amounted to 3.5, 9.7, and 24.7%, respectively.

The study of fractures of samples 2 revealed that their relief is similar to that of samples 1. Rows of elevations and hollows oriented normally to the applied force were observed. This orientation was more clearly expressed, since the plastic deformation increased due to an increase in the molding pressure from 50 to 100 MPa and the presence of PVA. The higher density of the preforms produced a decrease in shrinkage which after firing at the temperatures of 1300, 1500, and 1700°C amounted to 3.5, 9.4, and 22.5%, respectively. The main distinction was the fact that while the average size of the hollows in samples 2 was close to that of samples 1 (60 μm), samples 2 in addition exhibited larger elevations and hollows (100 μm). These large structural elements virtually disappeared at the temperatures of 1000 and 1100°C and reappeared at 1300 and 1500°C, reaching the size of 300 – 400 μm. After protracted firing at the temperature of 1700°C, no large structural elements were detected.

The fractures in samples 3 made of a plastic mixture significantly differed from the samples obtained by semidry compaction (1 and 2). The size of the elevations and hollows in a dried preform reached 600 μm, exhibited pores of irregular shape up to 120 μm and round pores 30 – 60 μm in size. No orientation was observed in the elevations and hollows. After heat treatment at 700°C, the maximum size of the hollows decreased to 150 μm. At the temperature of 1000°C, the fracture became even, and the hollow size was 25 – 30 μm. After firing at the temperature of 1100°C, the linear shrinkage of the samples amounted to 3%, and the size of the hollows once more increased to 600 μm. Heat treatment at 1300 and 1500°C produced shrinkage of 3 and 11%, respectively. The maximum size of the hollows at the temperature of 1300°C amounted to 450 μm, and at 1500°C it decreased to 150 μm. The size of the small-scale elevations and hollows at the temperatures of 1100, 1300, and 1500°C amounted to about 30 μm. After protracted firing at 1700°C, the fracture relief of all tested samples virtually coincided.

The experimental results confirm that even slight variations in the density of a preform (local compaction) which arise in molding can have a decisive effect on the evolution of the preform structure in the course of heating. The study of the surfaces of sample fractures revealed that local compaction areas already emerge in the molding stage. The structure of the fractures perceptibly differs depending on the molding method. A less pronounced and yet noticeable difference was caused by a variation in the molding pressure from 50 to 100 MPa.

The molding of non-granular highly disperse powder in a preform presumably produces hierarchically bound dissipative structures represented by local compaction areas. Under the effect of supplied energy, the system disintegrates into blocks which form a stronger skeleton absorbing the mechanical load and less dense areas. The formation of the skeleton enables the system to efficiently withstand deformation in the initial stage of compaction and to develop conditions for dissipating part of the energy on elastic deformation of the punches and matrix walls. The system virtually develops an infinite cluster penetrating the entire molded article. The process of formation of the infinite cluster is described by percolation theory. With an increase in the molding pressure, a continuous process of destruction and restoration of the skeleton cluster takes place, which results in its strengthening and compaction.

The elements of the skeleton cluster are granules which emerge in rubbing the powder with a binder through a sieve. The size of the granules is much smaller than the size of the sieve cells, since due to a deficit of binder, they disintegrate in rubbing and molding into smaller fragments. Although the initial strength of these granules is low, it can increase in compaction in the skeleton cluster. As a result, the skeleton cluster consists of primary compacted areas (granules) united into larger secondary structural elements.

Similar processes occur in drying of samples made of a plastic mixture. On removal of water, the system disintergates into local compaction areas united into larger structural elements whose size is much larger than in semidry compaction. Between the larger structural elements, the most weakened areas emerge, and it is precisely here that the crack passes through them. As a consequence, the fractures of dried preforms as well as preforms fired at a temperature below 1000°C exhibit fairly large elevations and hollows in their relief.

In heat treatment, local compaction (sintering) takes place. As follows from the experimental data, sintering first occurs in the smaller (primary) granules. Presumably, these granules can be turned to a certain extent in this process. Since the primary granules are not spheric, this turn produces an increase in the porosity inside the larger (secondary) compactions. The volume of the secondary compactions can increase as well, and they are squeezed more tightly against each other. This can be the reason for the levelling of the strgength of the secondary compactions and the boundaries between them. The levelling of strength can be also attributed to relaxation of the mechanical stresses arising in molding and drying and persisting up to high temperatures owing to the nonisometric shape of corundum crystals. Relaxation is facilitated by the anisotropy of the thermal coefficient of linear expansion of corundum and surface diffusion. A crack starts moving across the compactions, and the fracture becomes smoother. This was observed at the temperature of

1000 in samples 3 made by plastic molding. A similar situation occurred at the temperature of 1000 and 1100°C in samples 2 molded at a molding pressure of 100 MPa. It is precicely in this temperature region that the bifurcation presumably occurs which determines the subsequent structure of the preform.

Further heat treatment causes mutual scorching of the primary elements. The larger secondary compactions with weakened boundaries reappear once more, and the crack starts moving along these boundaries, which causes an increase in the size of the elevations and hollows on the fracture surface. This was observed in samples 3 at the temperatures of 1100, 1300, and 1500°C, and in samples 2 at 1300 and 1500°C. Further protracted firing at a high temperature (1700°C for 12 h) facilitates gradual healing of these boundaries. Their strength increases up to the strength of the primary granule boundaries along which the crack migrates. The fracture becomes smooth, with small elevations and hollows.

The emergence of density variations (local compactions) in molding is a bifurcation process, but in subsequent phases it can become the controlling effect. This fact determines the role of the inherited structure and properties in ceramic technology. Each preceding phase develops structures which in subsequent phases can control the evolution of the system. With a sufficiently great difference between the local compaction area density and the boundary area density, it can be inherited. This phenomenon has long been known and is used in development of heat-resistant fragmentary structures [5].

In order to prevent the effect of the initial structure (local compactions emerging in molding and drying), superfast sintering is successfully used [4]. In this case, the degree of nonequilibrium in the bifurcation region is so high that the internal fluctuations caused by sintering apparently become comparable to or exceed the level of the controlling signal of the preceding structure. An increase in the degree of process nonequilibrium in these circumstances produces a decrease in the size of the dissipative structural elements [1]. Ceramics produced by this method consist of small crystals of similar sizes [4].

High dispersion of the initial powder particles increases the sensitivity of the system (the preform in firing) to the controlling action of the local compactions existing within that system. In this case, in order to implement superfast sintering, the fluctuation amplitude should be increased through an increase in the degree of nonequilibrium (the preform heating rate). However, the degree of nonequilibrium of the energy supply in heat treatement cannot be as high as one would like. It is always limited by the preform size, heat conduction and heat resistance. As a result, the use of highly disperse powders inreases the possibility of inheritance of the structure. This is supported by the more obvious nature of the local compactions observed in samples made of powders prepared by chemical methods, whose crystal size is below 1 μm.

In plastic molding, a system is broken down into structural elements which are local compaction areas. Their size and shape can alter in molding. If the structural elements are shifted with respect to each other, shear planes emerge which are manifested in drying in the form of stress zones or even microcracks. It is exhibited on the fracture surface in the form of steps. As the amount of binder increases (within a certain interval), the possibility of shear increases and the steps on the fracture surface are more clearly expresssed. The formation of large structural elements is faciliated by insufficiently uniform distribution of the binder, since its amount is relatively low (compared to casting). However, the proper structural elements are laid in the stage of molding. In plastic molding, the system spontaneously disintegrates into structural elements.

The higher amount of binder used in casting results in the absence of structural elements similar to the elements emerging in plactic molding. The amount of binder is sufficiently high, and the binder is distributed more uniformly than in plastic molding. Transition to the plastic state proceeds rapidly, and though the system in molding splits into blocks, presumably they virtually never shift with respect to each other, as opposed to plastic molding. No microcracks arise in drying. As a result, no steps are observed on the fracture surface.

The proposed method of investigation of fracture surfaces confirmed that the structure of an article is created at the phase of molding and drying. The method makes it possible to determine the temperature region of bifurcation of the sintered system, when the fracture becomes smoother. Apparently, in determining the bifurcation region, it is not essential for a crack to pass precisely along the local compaction boundaries. It is enough for the crack to be to a certain extent "sensitive" to the compactions.

The use of the results of the study of fractures in technology opens the possibility of increasing the reproducibility of the structure of ceramic products. Processing of data can be significantly accelerated and performed more correctly using a computer. The published data mention programs which make it possible to obtain three-dimensional computer images of fractures and to analyze them [6], which significantly simplifies data interpretation.

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